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Kinetic Modelling of Non – Catalytic Pyrolysis of Waste Jute in a Fixed Bed Pyrolyzer

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Abstract

Waste jute has been investigated as an alternative feedstock for the generation of liquid and gaseous fuel through non – catalytic pyrolysis in a fixed bed reactor. Kinetic parameters for the pyrolysis of jute wastes have been determined in the temperature range of 400 – 900°C. A fixed bed reactor model has been developed using the kinetic parameters determined during the present study and the literature data on secondary tar cracking reaction.

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Keywords: pyrolysis kinetic, pyrolysis product yield, energy yield, jute.

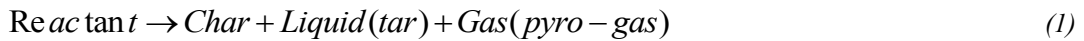
1. Introduction

Biomass is of major interest as a renewable energy source in the context of both climate change mitigation and energy security. Among the lignocellulosic wastes generated in India jute contributes a large portion. According to the jute packing material act enacted in 1987, entire quantities of food grains and sugar have to be compulsorily packed in jute sacks. Moreover, jute sacks are also used, to some extent, in cement industries. After utilization of the packed materials many of the jute sacks face disposal problem. Therefore, suitable waste to energy technology should be utilized to generate energy from waste jute sacks. Pyrolysis is a thermal degradation process which may be utilized for the generation of non-conventional energy resources from

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waste materials. The mechanism of primary pyrolysis of solid and liquid feed-stocks is as follows,



In recent years many works have been reported in the literature on pyrolysis of municipal solid wastes [1]-[8]. Although it is apparent that jute is one of the main contributors of lignocellulosic wastes in India, studies of pyrolysis of waste jute is however lacking. Under the present investigation, pyrolysis kinetics of waste jute sacks has been studied in the temperature range of 673K to 1173K. Lumped kinetic parameters have been determined. The yield and characteristics of pyro -oil have been determined. A mathematical model has been developed for a semi batch pyrolyser based on waste jute.

2. Experimental

Jute: Jute was collected from a local market. Table 1 summarizes the results of proximate analysis of the jute sample.

Table 1. Proximate analysis of Jute Fibres

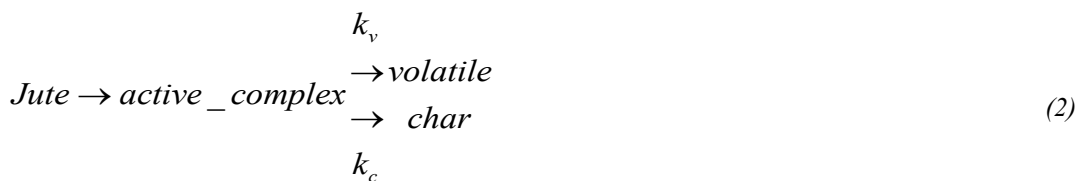
ProximateAnalysis	Moisture	Volatile Matter	Ash	Fixed Carbon
% (W/W)	10.025	77.15	2.59	10.235

A muffle furnace (Bhattacharya & Co. India) and a Bomb calorimeter (S. C. Dey & Co. India) were used. A CHNSO analyser (Perkin Elmer) and FTIR spectroscopy (SHIMADZU FTIR 8400) were used. The pyrolysis of jute sample has been done by following the procedure described in [2].

3. Theoretical Analysis

3.1. Pyrolysis Kinetics

Under the present study a parallel reaction model has been attempted to describe pyrolysis kinetics of jute wastes. According to this model pyrolysis of jute has been considered to be a homogeneous solid phase reaction and the pyrolysis products have been lumped as char – the solid product and volatiles made up of tar (condensable) and gaseous products. The volatile is further assumed to crack to different gaseous components, namely, CO, CO₂, H₂, CH₄ and inert tar. The reaction pathway of pyrolysis according to the present model is as follows,



Therefore,

$$\frac{dW}{dt} = -kW \quad (3a) \quad \frac{dW_v}{dt} = k_v W \quad (3b)$$

$$\frac{dW_c}{dt} = k_c W \quad (3c)$$

where $k = k_v + k_c$

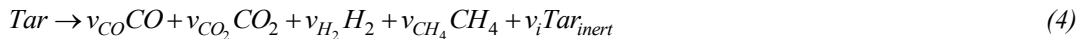
The rate constants k , k_v and k_c have been determined through non-linear regression analysis of

experimental data of captive sampling experiments [3], [4]. The frequency factors and activation energies are given in Table 2.

Table 2. Calculated Activation Energies and Frequency Factors as per Arrhenius Law

Reaction rate constant	K	k_v	k_c
Frequency Factor (min^{-1})	1.252323	23.5706	6.086054
Activation Energy (kJ/mol)	22.55588	50.6572	41.3374
Correlation coefficient	1	1	1

Among the volatile components, namely tar, CO, CO₂, H₂ and CH₄, tar generated from pyrolysis of jute is decomposed through a homogeneous tar cracking reaction. Tar cracking reaction may be represented as follows,



The stoichiometric coefficients, v_i have been reported Table 3.

The rate equation for tar cracking reaction is as follows,

$$\dot{r}_{j,\text{crack}} = v_j \cdot 10^{4.98} \cdot \exp\left(-\frac{93.37}{RT_{\text{par}}}\right) \cdot (W_{g,\text{tar}} \rho_g) \quad (5)$$

where, $(W_{g,\text{tar}} \rho_g)$ is the concentration of tar in the gas phase.

All alkanes and alkenes are lumped as methane. Secondary reactions among gaseous components are not being considered during this modelling.

3.2. Mathematical Model and Prediction

Based on the reaction kinetics [7] determined in the previous section a mathematical model has been developed to predict the gas phase composition of the pyrolysis products.

The mass balance equation for any volatile component “i” under dynamic condition is as follows,

$$\frac{\partial}{\partial t}(\varepsilon \cdot \rho w_{vi}) = -\frac{\partial}{\partial z}(v \varepsilon \rho w_{vi}) + \varepsilon D_{gi} \rho \frac{\partial^2 w_{vi}}{\partial z^2} + \sum_{j=1}^n r_{ij} \quad (6)$$

Where, i = tar or CO or CO₂ or H₂ or CH₄.

The values of diffusivities, D_{gi} of all gaseous components have been provided in Table 3. The term on the left hand side of the above equation represents accumulation, 1st, 2nd and 3rd terms on the right hand side of the equation represent convective flow component, dispersive flow component and the reactive part consisting of reactions (j) of all types, namely reaction-I and II involving the component “i”. The mass balance equations (6) for all components have been solved numerically using MATLAB function pde4.

3.3. Energy Yield

The energy yield of pyro – oil obtained at different pyrolysis temperature have been determined using the following correlation,

$$\text{EnergyYield (\%)} = \frac{w_i X CV_{oil}}{CV_{jute}} X 100 \quad (7)$$

where, w_i = yield (weight fraction) of pyro – oil ,
 CV_{oil} = Calorific Value of pyro – oil (MJ/Kg)
 CV_{jute} = Calorific Value of jute (MJ/Kg)

4. Result and Discussions

4.1. Trend of pyrolysis product yield and product characteristics.

From the analysis of experimental data, it was observed (not shown) that yield of char increased upto 873K after which it remained constant. On the other hand yield of tar increased in the entire range of pyrolysis temperature from 673K to 1173K. Yield of gas was observed to increase from 673K to 973K after which it remained constant up to 1173K. The yield of volatiles again showed an increasing trend in the temperature range of 673K to 1173K. The pH values of the tar were found to be in the range of 4 – 5. The calorific values of pyro – oil varied from 16.924 to 31.545 MJ/kg as the pyrolysis temperature was increased from 673K to 1173K.

4.2. Fourier Transform Infrared Spectroscopy (FTIR) Analysis of jute Tar

The functional groups of the pyro – oil obtained at temperature of 700°C was analyzed by Fourier Transform Infrared (FTIR) spectroscopy to identify the basic compositional groups. Based on the FTIR results, the functional groups and the indicated composition of the liquid products are presented in Table 4. The table shows the presence of alkanes, alkenes, ketones, aldehydes and carboxylic acids, primary, secondary and tertiary alcohols, ethers and esters, single, polycyclic and substituted aromatics groups and the presence of water impurities and other polymers.

Table 3. Values of diffusivities of tar and components of pyro – gas

Component	Tar	Tar_{inert}	CO	CO ₂	H ₂	CH ₄
Diffusivity (m ² /s)	10 ⁻⁶	0	19 X 10 ⁻⁶	14 X 10 ⁻⁶	78 X 10 ⁻⁶	16 X 10 ⁻⁶
v_i	1	0.22	0.78 X 0.72222	0.78 X 0.14222	0.78 X 0.02222	0.78 X 0.11334

Table 4. FTIR functional groups and the indicated compounds of jute Tar

Frequency Range (cm ⁻¹)	3600 – 3200	3050 – 2800	1775 – 1650	1680 – 1575	1570 – 1475	1490 – 1325	1300 – 950	900 – 650
Groups	O – H stretching	C – H stretching	C = O stretching	C ≡ C stretching	-NO ₂ stretching	C – H stretching	C – O stretching, O – H bending	-
Class of compounds	Polymeric O – H	Alkanes	Ketones, Aldehydes, Carboxylic acids	Alkenes	Nitrogenous compounds	Alkanes	Primary, Secondary and Tertiary alcohols, Phenols, esters, ethers	Aromatic compounds

The pronounced oxygenated functional groups of O – H; C = O; C – O and aromatic compounds show that the oil is highly oxygenated and therefore, very acidic, as have also been indicated by the elemental composition and the pH value. The high fraction of oxygenated compounds reduces the calorific value of the oil since C = O bonds do not release energy during combustion. The presence of hydrocarbon groups C – H; C = C; and alcohols indicate that the liquids have a potential to be used as fuel. The results of FTIR analysis is comparable to those obtained [1] during their studies on pyrolysis of jute wastes.

4.2.1 Time Histories of Weight fraction of residue during captive sampling Experiments

Figure 2 shows the experimental weight fraction profile of pyrolysis residue with respect to time in isothermal conditions from 673K to 1173K. From close observation of the data, it appears that the pyrolysis reactions proceed considerably in the temperature range of 573K to 1173K. Below this temperature range the reactions do not occur at an appreciable rate.

From the plots, it is also apparent that at each temperature, a quasi – equilibrium of the reaction prevails. The rates of devolatilization reactions decline at temperatures above 673K. Therefore, the values of frequency factors and activation energies of the reactions of reactant decomposition, volatile formation and char formation are determined by regression analysis of the rate constant determined in the temperature range of 573K to 673K [3], [4]. The frequency factors and activation energies of different reactions are given in Table 3.

4.3. Results of Model Simulation

In Figure 3 the mass fraction of tar in the gas phase has been plotted against reaction time at 700°C with the axial position as a parameter. It is evident that the maximum fraction of reactive tar in the gaseous phase is 31% whereas those (not shown) of CO₂, H₂, CO and CH₄ are 11, 0.1, 2, 1.75 % respectively. These are also in agreement with the experimental values.

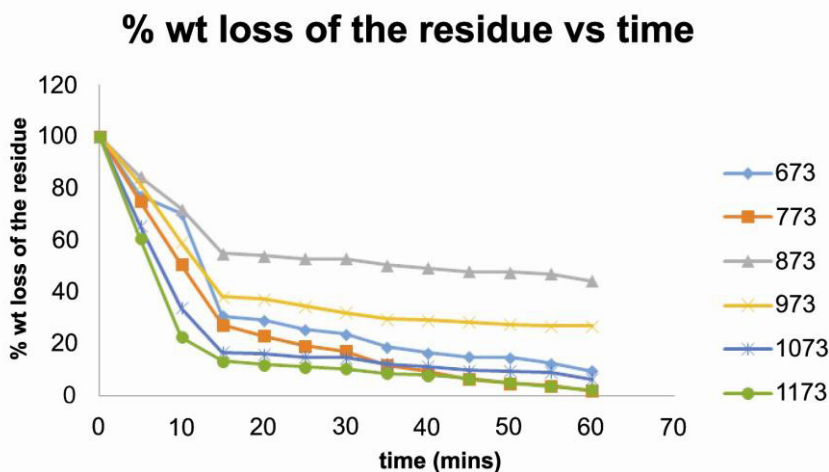


Fig. 1. Variation of percentage of weight of residue of textile wastes sample with respect to time at different pyrolysis temperature

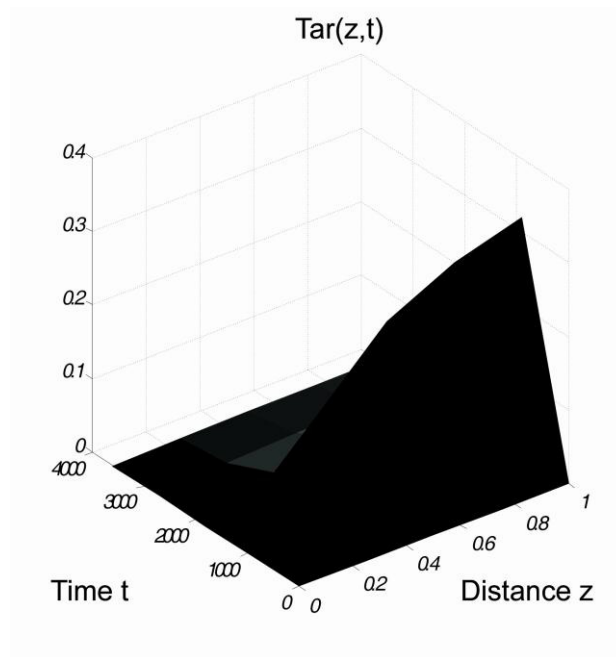


Fig. 2. The mass fraction of tar plotted against reaction time with the axial position as a parameter.

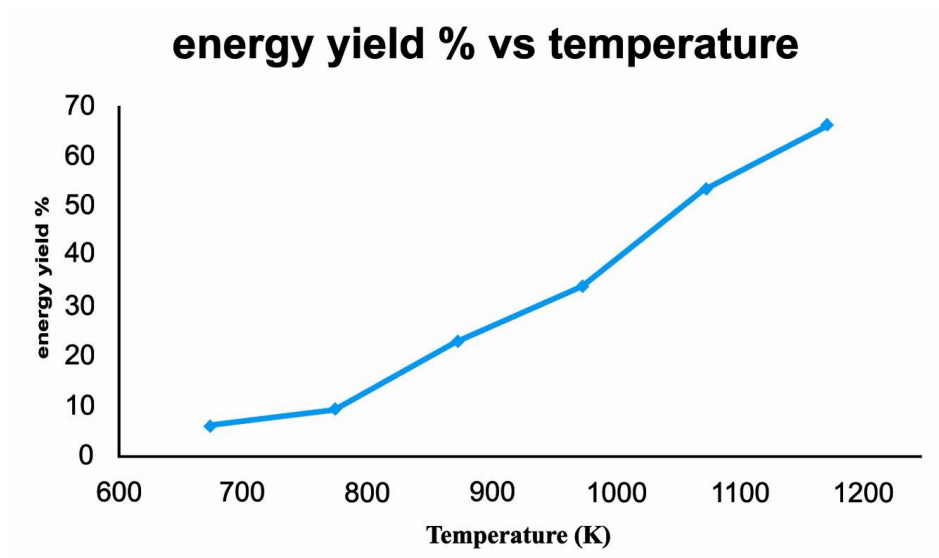


Fig. 3. Variation of energy yield (%) with temperature.

4.4. Energy Yield

The values of energy yield of pyro – oil have been plotted against pyrolysis temperature in figure 3. From

the analysis of the figure it appears that the increase in pyrolysis temperature results in the increase of energy yield with respect to pyro-oil. It may be due to the fact that with the increase of pyrolysis temperature the tar becomes richer in carbon which leads to the increase in specific energy content.

5. Conclusion

Pyrolysis kinetics of waste jute materials has been determined. A mathematical model involving partial differential equations for axial distribution of gaseous components under transient condition has been developed using the kinetic parameters determined during this study and the literature data on cracking kinetics of tar. The model can predict the behaviour of the semi- batch pyrolyzer under dynamic condition. The model may be utilized for further studies on pyrolysis using similar biomass feed stocks.

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